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AMENDED SPECIFICATION

Reprinted as amended in accordance with the Decision of the Superintending Examiner, acting for the Comptroller-General, dated the eleventh day of October, 1952, under Section 14 of the Patents Act, 1949.

PATENT SPECIFICATION

636,429



Date of filing Complete Specification (under Section 16 of the Patents and Designs Acts, 1907 to 1946): Nov. 30, 1948.

Application Date: Dec. 1, 1947. No. 31661/47.

Application Date: April 21, 1948. No. 10996/48.

Application Date: April 21, 1948. No. 10997/48.

Complete Specification Published: April 26, 1950

Index at acceptance:—Classes 2(iii), C3a(7: 10e4); and 2(v), R3d(1: 2: 4: 6), R3m(1: 4), R9(m: p).

PROVISIONAL SPECIFICATION

No. 31661 A.D. 1947.

Improvements in and relating to the Production of Polymeric Esters

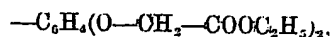
We, **COURTAULDS LIMITED**, a British Company, of 16, St. Martin's-le-Grand, in the City of London, **ERIC RICHARD WALLSGROVE**, a British Subject, of 105, Baginton Road, Coventry, in the County of Warwick, and **FRANK REEDER**, a British Subject, of 495, Gower Road, Killay, Swansea, in the County of Glamorgan, do hereby declare the nature of this invention to be as follows:—

This invention relates to the production of polymeric esters.

A process has been described by Bischoff and van Hederstrom in *Berichte*, Volume 35, (1902) for the manufacture of hydroquinone esters by heating hydroquinone and a diphenyl ester at 170° to 250° Centigrade; thus hydroquinone and diphenyl carbonate are reported on page 3431 to yield hydroquinone carbonate, hydroquinone and diphenyl oxalate are reported on page 3454 to yield hydroquinone oxalate and hydroquinone and diphenyl succinate are reported on page 4073 to yield hydroquinone succinate.

W. H. Carothers, in the *Journal of the American Chemical Society*, Volume 57 (1935) pages 935—6 reported that polymeric esters which are capable of being depolymerised to yield cyclic monomers are obtained by esterifying the acids *m* and *p* C₆H₄(O—CH₂—COOH)₂ with glycols of the series HO(CH₂)_nOH. In the case of the hydroquinone polyesters, it is also reported that owing to the high melting point of the acid the ester ethyl

hydroquinone diacetate



was condensed with the glycol.

In United States Patent No. 2,284,637 it is proposed to prepare polymeric carbamates by condensing a diisocyanate or a diisothiocyanate with a dihydric alcohol, a dithiol, or a dihydric phenol. French Specification No. 866,821 describes the manufacture of polyamides of high molecular weight by condensing a bifunctional compound containing amino, hydroxyl, acetylatable sulph-hydryl or carboxylic groups with a compound containing at least one carbamic acid radical esterified with a benzoid or enolic hydroxyl compound.

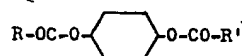
The object of the present invention is to produce improved polymeric esters which are suitable for the preparation of fibres capable of being cold drawn.

In accordance with the present invention, a process for the production of polymeric esters comprises condensing an *o,o'*-dicarboxylic acid or terephthalic acid, or a bifunctional derivative of such acids with a diester of an aliphatic monocarboxylic acid and an aromatic dihydroxy compound in which the hydroxy groups if on the same benzene nucleus are in the *p* position with respect to each other, and if on different benzene nuclei are in the *p* and *p'* positions.

Suitable *o,o'*-dicarboxylic acids for use

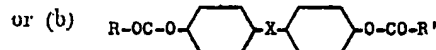
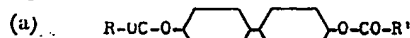
in accordance with the present invention are those having the general formula $\text{HOOC}-(\text{CH}_2)_n-\text{COOH}$, n being an integer from 0 to 12; specific examples 5 are oxalic acid, succinic acid, adipic acid and sebacic acid. Bifunctional derivatives of the acids, for example the acid chlorides or anhydrides, may also be used; bifunctional compounds are defined 10 by W. H. Carothers in the Journal of the American Chemical Society, volume 51 (1929) pages 2548-59 as compounds of the type $x-\text{R}-x$, $y-\text{R}-y$, $x-\text{R}-y$ wherein R stands for a bivalent radicle and x and y are functional groups 15 capable of interacting to form a new grouping.

Suitable diesters for use in the present invention are the diesters of hydroquinone 20 having the general formula



in which R and R' are the same or

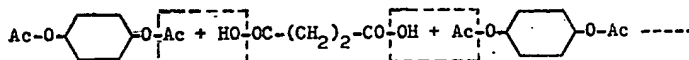
different alkyl groups. Other diesters which may be used are those having the general formulae:— 2



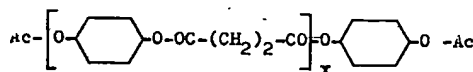
in which R and R' are the same or different alkyl groups and X is a bivalent linking group such as $-\text{O}-$, $-\text{S}-$, $-\text{CO}-$, $-\text{O}-(\text{CH}_2)_l-\text{O}-$, or $-(\text{CH}_2)_m-$, l and m being whole integers. 30

The reaction of the present invention proceeds by elimination of a fatty acid. Thus for example with hydroquinone 3 diacetate and succinic acid, acetic acid is evolved and it is believed that a polymer is built up by a sequence of reactions as follows:—

40



and the polymer is therefore believed to have the formula:—



x being a large number.

It is preferable that a lower fatty acid ester such as the acetate be used in order that the acid formed may be removed readily by distillation during the reaction which normally takes place at or above 180° Centigrade. 45

The reaction is preferably effected in the absence of air to oxygen for example by passing an inert gas such as nitrogen, hydrogen or carbon monoxide into the reaction mixture. A condensation 50 catalyst, for example *p*-toluene sulphonic acid is preferably also added to the reaction mixture.

The polymeric esters obtained by the present invention may be melt-spun 60 through nozzles to form fibres which can be cold drawn to give oriented fibres exhibiting crystalline X-ray photographs.

The invention is illustrated by the following Examples in which the parts 65 are by weight.

EXAMPLE 1.

Hydroquinone diacetate, $\text{C}_6\text{H}_4(\text{O}-\text{CO}-\text{CH}_3)_2$, was prepared from hydroquinone and acetic anhydride in the presence of caustic soda by the method described by F. D. Chattaway in the Journal of the Chemical Society, September 1931, pages 2495-6. 10 parts of the hydroquinone diacetate were then mixed with 9.5 parts of succinic acid and 0.1 part of *p*-toluene sulphonic acid and the mixture was heated in a stream of nitrogen at atmospheric pressure at 180° Centigrade for 45 minutes, at the end of which time the evolution 8 of acetic acid had ceased. The reaction mixture was then heated under nitrogen at 200° to 220° Centigrade for 1 hour, and at 280° Centigrade for 3 hours, all at atmospheric pressure, and finally was 8 heated at 280° Centigrade under mercury pressure of 1 m.m. for 3 hours while nitrogen was being bubbled through the

molten reaction mixture.

The polymeric hydroquinone succinate obtained was melt-spun into fibres which could be cold drawn. The stretched fibres were pliable and gave a crystalline X-ray photograph.

EXAMPLE 2.

Example 1 was repeated with the difference that the 9.5 parts of succinic

acid were replaced by the corresponding 10 quantity (14 parts) of adipic acid to yield to polymeric hydroquinone adipate.

Dated this 1st day of December, 1947.

J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields,
London, W.C.2,
Chartered Patent Agents.

PROVISIONAL SPECIFICATION

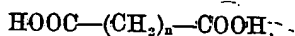
No. 10996 A.D. 1948.

Improvements in and relating to the Production of Polymeric Esters

We, COURTAULDS LIMITED, a British Company, of 16, St. Martin's-le-Grand, in the City of London, ERIC RICHARD WALLSGROVE, a British Subject, of 105, Baginton Road, Coventry, in the County of Warwick, and FRANK REEDER, a British Subject, of 495, Gower Road, Killay, Swansea, in the County of Glamorgan, do hereby declare the nature of this invention to be as follows:—

This invention relates to the production of polymeric esters.
In the specification of our application No. 31661/47 we have described a process for the production of polymeric esters comprising condensing an ω,ω' -dicarboxylic acid or terephthalic acid, or a bifunctional derivative of such acids with a diester of an aliphatic monocarboxylic acid and an aromatic dihydroxy compound in which the hydroxy groups if on the same benzene nucleus are in the p position with respect to each other, and if on different benzene nuclei, are in the p and p' positions.

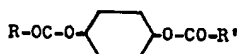
Suitable ω,ω' -dicarboxylic acids for use in the process of our said specification No. 31661/47 are stated to be those having the general formula



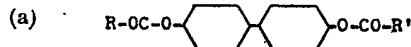
n being an integer from 0 to 12; specific examples are oxalic acid, succinic acid, adipic acid and sebacic acid. Bifunctional derivatives of the acids, for example the acid chlorides or anhydrides, may also be used; bifunctional compounds are defined by W. H. Carothers in the Journal of the American Chemical Society, volume 51 (1929) pages 2548—59 as compounds of the type $x-\text{R}-y$ and $x'-\text{R}'-y'$ wherein R stands for a bivalent radicle and x and y are functional groups capable of interacting to form a new grouping.

Suitable diesters described are the di-

esters of hydroquinone having the general formula



in which R and R' are the same or different alkyl groups. Other diesters which may be used are those having the general formulae:—



in which R and R' are the same or different alkyl groups and X is a bivalent linking group such as $-\text{O}-$, $-\text{S}-$, $-\text{CO}-$, $-\text{O}-(\text{CH}_2)_l-\text{O}-$, or $-(\text{CH}_2)_m-$, l and m being whole integers.

It is also stated that the reaction proceeds by elimination of the fatty acid and that the lower fatty acid ester such as the acetate is preferably used in order that the acid formed may be removed readily by distillation during the reaction which normally takes place at or above 180° Centigrade. The reaction is preferably effected in the absence of air or oxygen for example by passing an inert gas such as nitrogen, hydrogen or carbon monoxide into the reaction mixture. A condensation catalyst, for example p -toluene sulphonic acid is preferably also added to the reaction mixture.

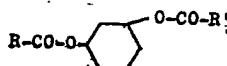
It is further stated that the polymeric esters obtained may be melt-spun through nozzles to form fibres which can be cold drawn to give oriented fibres exhibiting crystalline X-ray photographs.

We have now found that the process described in our said specification No. 31661/47 may also be carried out with diesters of an aliphatic monocarboxylic

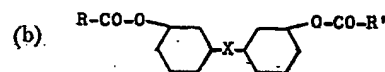
acid and an aromatic dihydroxy compound in which the hydroxy groups, if on the same benzene nucleus, are in the *m* position with respect to each other, or if on different benzene nuclei, are in the *m* and *m'* positions.

In accordance with the present invention, therefore, a process for the production of polymeric esters comprises condensing an ω,ω' -dicarboxylic acid or terephthalic acid, or a bifunctional derivative of such acids with a diester of an aliphatic monocarboxylic acid and an aromatic dihydroxy compound in which the hydroxy groups, if on the same benzene nucleus, are in the *m* position with respect to each other, or if on different benzene nuclei, are in the *m* and *m'* positions.

Suitable diesters for use in the present invention are the diesters of resorcinol having the general formula:—



in which R and R' are the same or different alkyl groups. Other diesters which may be used are those having the general formulae:—



in which R and R' are the same or different alkyl groups and X is a bivalent linking group such as —O—, —S—, —CO—, —O—(CH₂)_l—O—, or —(CH₂)_m—, l and m being whole integers.

The present invention is illustrated by the following Example in which the parts are by weight:—

EXAMPLE.

20.1 parts of resorcinol diacetate (prepared from resorcinol and acetic anhydride in the presence of caustic soda by the method described by F. D. Chattaway in the Journal of the Chemical Society, September 1931, pages 2495—6), 15.0 parts of succinic acid and 0.06 parts of *p*-toluene sulphonic acid were heated to 200° Centigrade in a stream of oxygen-free nitrogen. The temperature was then raised to 280° Centigrade over a period of 2 hours at the end of which time the evolution of acetic acid had ceased. The temperature was then reduced to 270° Centigrade, the pressure reduced to 12mm. of mercury and heating was continued for 1 hour, a stream of oxygen-free nitrogen being bubbled through the melt continuously. The product obtained was a polymeric resorcinol succinate, melting at about 260° Centigrade and fibres, capable of being cold drawn, were drawn from the melt.

Dated this 21st day of April, 1948.

J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields;
London, W.C.2,
Chartered Patent Agents.

PROVISIONAL SPECIFICATION

No. 10997 A.D. 1948.

Improvements in and relating to the Production of Polymeric Esters

We, COURTAULDS LIMITED, a British Company, of 16, St. Martin's-le-Grand, in the City of London, ERIC RICHARD WALLSGROVE, a British Subject, of 105, Baginton Road, Coventry, in the County of Warwick, and FRANK REEDER, a British Subject, of 495, Gower Road, Killay, Swansea, in the County of Glamorgan, do hereby declare the nature of this invention to be as follows:—

This invention relates to the production of polymeric esters.

In the specification of our application No. 31661/47 we have described a process for the production of polymeric esters comprising condensing an ω,ω' -dicarboxylic acid or terephthalic acid, or a

bifunctional derivative of such acids with a diester of an aliphatic monocarboxylic acid and an aromatic dihydroxy compound in which the hydroxy groups if on the same benzene nucleus are in the *p* position with respect to each other, and if on different benzene nuclei, are in the *p* and *p'* positions.

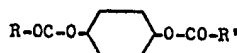
Suitable ω,ω' -dicarboxylic acids for use in the process of our said specification No. 31661/47 are stated to be those having the general formula



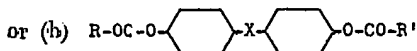
n being an integer from 0 to 12; specific

examples are oxalic acid, succinic acid, adipic acid and sebacic acid. Bifunctional derivatives of the acids, for example the acid chlorides or anhydrides, may also be used; bifunctional compounds are defined by W. H. Carothers in the Journal of the American Chemical Society, volume 51 (1929) pages 2548-59 as compounds of the type $x-R-x$ and $x-R-y$ wherein R stands for a bivalent radicle and x and y are functional groups capable of interacting to form a new grouping.

Suitable diesters described are the diesters of hydroquinone having the general formula



in which R and R' are the same or different alkyl groups. Other diesters which may be used are those having the general formulae:—



in which R and R' are the same or different alkyl groups and X is a bivalent linking group such as $-O-$, $-S-$, $-CH_2-$, $-O-(CH_2)_l-O-$, $-CO-$, $-O-(CH_2)_m-O-$, or $-(CH_2)_m-$, l and m being whole integers.

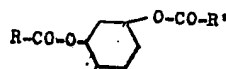
It is also stated that the reaction proceeds by elimination of the fatty acid and that a lower fatty acid ester such as the acetate is preferably used in order that the acid formed may be removed readily by distillation during the reaction which normally takes place at or above 180° Centigrade. The reaction is preferably effected in the absence of air or oxygen for example by passing an inert gas such as nitrogen, hydrogen or carbon monoxide into the reaction mixture. A condensation catalyst, for example p-toluene sulphonic acid is preferably also added to the reaction mixture.

It is further stated that the polymeric esters obtained may be melt-spun through nozzles to form fibres which can be cold drawn to give oriented fibres exhibiting crystalline X-ray photographs.

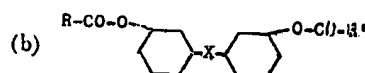
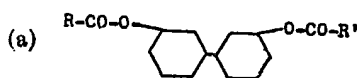
In the specification of our co-pending application No. 10996/48 of even date, we have described a process for the production of polymeric esters comprising condensing an ω,ω' -dicarboxylic acid, or terephthalic acid, or a bifunctional derivative of such acids with a diester of an aliphatic monocarboxylic acid and an

aromatic dihydroxy compound in which the hydroxy groups, if on the same benzene nucleus, are in the m position with respect to each other, or if on different benzene nuclei, are in the m and m' positions.

Suitable diesters described for use in the process of our said specification No. 10996/48 are the diesters of resorcinol having the general formula:—



in which R and R' are the same or different alkyl groups. Other diesters which may be used are those having the general formulae:—



in which R and R' are the same or different alkyl groups and X is a bivalent linking group such as $-O-$, $-S-$, $-CH_2-$, $-O-(CH_2)_l-O-$, or $-(CH_2)_m-$, l and m being whole integers.

We have now found that improved products may be obtained of the aromatic dihydroxy compounds employed in the processes described in our said specifications Nos. 31661/47 and 10996/48 are replaced in part by one or more ω,ω' aliphatic dihydroxy compounds or the mono- or di-esters of such compounds.

In accordance with the present invention therefore a process for the production of polyesters comprises condensing

(a) an ω,ω' -dicarboxylic acid or terephthalic acid, or a bifunctional derivative of such acids,

(b) an ω,ω' aliphatic dihydroxy compound or a mono- or di-ester of such a compound and

(c) a diester of an aliphatic monocarboxylic acid, and an aromatic dihydroxy compound in which the hydroxy groups, if on the same benzene nucleus, are in the m or p position with respect to each other, and, if on different benzene nuclei, are in the p and p' positions, or the m and m' positions. Suitable diesters falling within group (c) are those referred to in our said specifications Nos. 31661/47 and 10996/48 and specified above.

In carrying out the process according

to the invention the compounds belonging to groups (a), (b) and (c) as defined may be heated together; alternatively, the acid belonging to group (a) may be pre-
 5 condensed with either of the compounds in group (b) or group (c) and the pre-condensate subsequently condensed with the compound from the other group.

Suitable ω,ω' -dihydroxy compounds for
 10 use in the present invention are ethylene glycol, the polyethylene glycols such as triethylene glycol and tetraethylene glycol, and butane diol; alternatively, the mono- and di-esters of these compounds,
 15 for example the monoacetates and diacetates may be used. The diacetates are the preferred compounds.

The process according to the invention permits the production of polymers which
 20 are less brittle at ordinary temperatures and have lower melting points than the corresponding polymers prepared in the absence of the ω,ω' dihydroxy compound as defined.

The present invention is illustrated by the following Examples, in which the parts are by weight:—

EXAMPLE 1.

5.61 parts of ethylene glycol diacetate,
 30 26.2 parts of succinic acid and 0.15 part of *p*-toluene sulphonic acid were heated at 200° Centigrade for 1 hour in a stream of oxygen-free nitrogen. 30 parts of hydroquinone diacetate were then added
 35 and the heating continued at 210°

Centigrade for 30 minutes. The temperature was then slowly raised to 280° Centigrade and the pressure reduced to less than 1 mm. of mercury over a period of two hours, nitrogen being bubbled
 4 through the melt continuously through a capillary. The heating at 280° Centigrade and 1 mm. mercury pressure was continued for 5 hours. The product had a melting point of about 250° Centigrade
 4 and fibres, capable of being cold drawn were drawn from the melt.

EXAMPLE 2.

11.3 parts of ethylene glycol diacetate, 19.2 parts of succinic acid and 0.11 part
 5 of *p*-toluene sulphonic acid were heated at 190 to 210° Centigrade for 90 minutes in a stream of oxygen-free nitrogen. 15 parts of hydroquinone diacetate were then added and the heating continued at
 5 200° Centigrade for 15 minutes. The temperature was then raised to 240° Centigrade and the pressure reduced to less than 1 mm. of mercury over a period
 6 of 90 minutes, nitrogen being bubbled through the melt continuously through a capillary. Heating at 240° Centigrade and 1 mm. mercury pressure was continued
 6 for 5 hours. The product was a viscous liquid resin at ordinary temperatures. 6

Dated this 21st day of April, 1948.

J. Y. & G. W. JOHNSON,

47, Lincoln's Inn Fields,

London, W.C.2,

Chartered Patent Agents.

COMPLETE SPECIFICATION

Improvements in and relating to the Production of Polymeric Esters

We, COURTAULDS LIMITED, a British Company, of 16, St. Martin's-le-Grand, in the City of London, ERIC RICHARD WALLSGROVE, a British Subject, of 105, Baginton Road, Coventry, in the County
 70 of Warwick, and FRANK REEDER, a British Subject, of 495, Gower Road, Killay, Swansea, in the County of Glamorgan, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the production
 80 of polymeric esters.

A process has been described by Bischoff and van Hedenstrom in Berichte, Volume 35, (1902) for the manufacture of hydroquinone esters by heating hydro-
 85 quinone and a diphenyl ester at 170° to 250° Centigrade; thus hydroquinone and diphenyl carbonate are reported on page 3431 to yield hydroquinone carbonate.

hydroquinone and diphenyl oxalate are reported on page 3454 to yield hydro-
 9 quinone oxalate and hydroquinone and diphenyl succinate are reported on page 4073 to yield hydroquinone succinate.

W. H. Carothers, in a series of papers, re-published in book form under the title
 9 "High Polymers" Volume I, has described and discussed polyesterification reactions including that between dibasic acids and dihydric alcohols; in the
 10 Journal of the American Chemical Society, Volume 57 (1935) pages 935-6 he reported that polymeric esters which are capable of being depolymerised to yield cyclic monomers are obtained by
 1 esterifying the acids *m* and *p*



with glycols of the series $\text{HO}(\text{CH}_2)_n\text{CH}_2\text{OH}$. In the case of the polyesters derived from hydroquinone, it is also reported that

owing to the high melting point of the acid the diphenyl ester of hydroquinone diacetic acid $C_6H_4(O-CH_2-COOC_2H_5)_2$ was condensed with the glycol. This paper also appears on pages 259-262 of "High Polymers", Volume I.

In United States Patent Specification No. 2,284,637 it is proposed to prepare polymeric carbamates by condensing a diisocyanate or a diisothiocyanate with a dihydric alcohol, a dithiol, or a dihydric phenol. French Specification No. 866,821 describes the manufacture of polyamides of high molecular weight by condensing a bifunctional compound containing amino, hydroxyl, acetyltable sulphhydryl, or carboxylic groups with a compound containing at least one carbamic acid radical esterified with a benzoid or enolic hydroxyl compound.

United States Patent Specification No. 2,035,578 describes the production of ester-type synthetic resins by reacting a polyhydric phenol and a dibasic acid chloride.

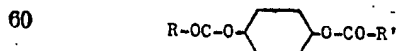
The object of the present invention is to produce mixed polymeric esters.

In accordance with the present invention a process for the production of mixed polymeric esters comprises condensing (a) an ω,ω' dicarboxylic acid or terephthalic acid, or an ester or anhydride of such acids, (b) a diester of an aliphatic monocarboxylic acid and an aromatic dihydroxy compound in which the hydroxy groups if on the same benzene nucleus are in the *p* or *m* position with respect to each other, and if on different benzene nuclei are in the *p* and *p'* or *m* and *m'* positions, and (c) an ω,ω' aliphatic dihydroxy compound, or a monoester or diester of such a compound.

Suitable ω,ω' dicarboxylic acids for use in accordance with the present invention are those having the general formula $HOOC-(CH_2)_n-COOH$, *n* being an integer from 0 to 12; specific examples are succinic acid, adipic acid, suberic acid and sebacic acid.

The anhydrides or esters of these acids may also be used; malonic acid which is decomposed on heating 132° Centigrade should preferably be used in the form of an ester.

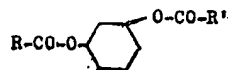
Suitable aromatic diesters for use in the present invention are the diesters of hydroquinone having the general formula



in which R and R' are the same or different alkyl groups. Specific examples

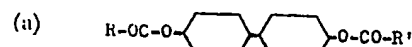
are hydroquinone diacetate, hydroquinone dipropionate and hydroquinone dibutyrate.

The diesters of resorcinol having the general formula



in which R and R' are alkyl groups, may also be used. Specific examples are resorcinol diacetate, resorcinol dipropionate and resorcinol dibutyrate.

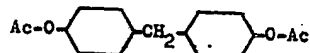
Other aromatic diesters which may be used are those having the general formulae:—



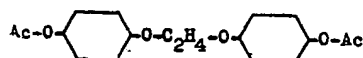
in which R and R' are alkyl groups and X is a bivalent linking group of the type $-\text{CH}_2-$, $-(\text{CH}_2)_2-$, $-\text{O}-$, $-\text{S}-$, $-\text{CO}-$, $-\text{O}-\text{CH}_2-\text{O}-$, or $-\text{O}-(\text{CH}_2)_2-\text{O}-$. Examples of these types of diesters are the esters of *p,p'* dihydroxy diphenyl, for example *p,p'* diacetoxo diphenyl which has the formula



the esters of *p,p'* dihydroxydiphenyl methane, for example *p,p'* diacetoxo diphenyl methane which has the formula



and the esters of *p,p'* dihydroxydiphenoxy ethane, for example *p,p'* diacetoxo diphenoxy ethane, which has the formula



The corresponding *m,m'* compounds may also be used.

When using the free dicarboxylic acid as compound (a), the reaction of the present invention proceeds by elimination of a fatty acid.

It is preferred that the aromatic di-ester employed in the invention should be an ester of a lower fatty acid, that is, a fatty acid containing not more than 6, preferably not more than 4, carbon atoms in the molecule, for example acetic acid, in order that the acid formed can be removed readily by distillation during the reaction which normally takes place at or above 180° Centigrade. When an ester of the dibasic acid is used, the corresponding fatty acid ester is eliminated.

In carrying out the process according to the invention the compounds belonging to groups (a), (b) and (c) as defined may be heated together; alternatively, the acid belonging to group (a) may be pre-condensed with either the compounds in group (b) or group (c) and the precondensate subsequently condensed with the compound from the other group.

Suitable aliphatic ω,ω' dihydroxy compounds for use in the present invention are ethylene glycol the polyethylene glycols such as triethylene glycol and tetraethylene glycol, propane 1,3 diol, butane 1,4 diol, pentane 1,5 diol and hexane 1,6 diol; alternatively, the mono- and diesters of these compounds, for example the monoacetates and diacetates may be used. The diacetates are the preferred compounds.

The reaction is preferably effected in the absence of air or oxygen for example by passing an inert gas such as nitrogen or hydrogen over or into the reaction mixture. A condensation catalyst, for example *p* toluene sulphonic acid or sulphuric acid is preferably also added to the reaction mixture.

The condensation according to the invention may be readily effected by heating the reactants together for example to temperatures of 200° Centigrade or higher. After the bulk of the fatty acid, or the corresponding acid derivative has been driven off, it is preferred to heat the mixture at a higher temperature, for example at temperatures of 240° to 280° Centigrade to complete the condensation; for all or part of this further heating operation, the pressure may be reduced.

The present invention is illustrated by the following Examples in which the parts are by weight:—

EXAMPLE 1.

5.65 parts of ethylene glycol diacetate, 26.2 parts of succinic acid and 0.15 part of *p*-toluene sulphonic acid were heated at 200° Centigrade for 1 hour in a stream

of oxygen-free nitrogen. 30 parts of hydroquinone diacetate were then added and the heating continued at 210° Centigrade for 30 minutes. The temperature was then slowly raised to 280° Centigrade and the pressure reduced to less than 1 mm. of mercury over a period of two hours, nitrogen being bubbled through the melt continuously through a capillary. The heating at 280° Centigrade and at a pressure of 1 mm. of mercury was continued for 5 hours. The product had a melting point of about 250° Centigrade and fibres were drawn from the melt.

EXAMPLE 2.

11.3 parts of ethylene glycol diacetate, 19.2 parts of succinic acid and 0.11 part of *p*-toluene sulphonic acid were heated at 190° to 210° Centigrade for 90 minutes in a stream of oxygen-free nitrogen. 15 parts of hydroquinone diacetate were then added and the heating continued at 200° Centigrade for 15 minutes. The temperature was then raised to 240° Centigrade and the pressure reduced to less than 1 mm. of mercury over a period of 90 minutes, nitrogen being bubbled through the melt continuously through a capillary. Heating at 240° Centigrade and at a pressure of 1 mm. of mercury was continued for 5 hours. The product was a viscous liquid resin at ordinary temperatures.

EXAMPLE 3.

9.05 parts of triethylene glycol diacetate, 26.2 parts of succinic acid and 0.11 part of *p*-toluene sulphonic acid were mixed together and heated for 20 minutes at a temperature rising from 200° to 230° Centigrade and at atmospheric pressure; 30 parts of hydroquinone diacetate were added and heating continued for 20 minutes at 200° to 220° Centigrade and at atmospheric pressure. The pressure was then reduced over a period of 105 minutes to 0.5 mm. of mercury the temperature being maintained at 220° to 240° Centigrade. The mixture was then heated at this pressure for 3 hours at a temperature rising from 240° to 280° Centigrade followed by 7½ hours at 280° Centigrade. The heating was conducted throughout under oxygen-free nitrogen as in the previous Examples.

The polymeric product was rubbery at 150° Centigrade but above this temperature it could be spun into fibres; its intrinsic viscosity in meta-cresol was 0.31.

In this specification, intrinsic viscosity is defined as:—

log. relative viscosity

concentration in grams per 100 cc. solution

EXAMPLE 4.

3.6 parts of pentane 1:5 diol diacetate, 12.8 parts of succinic acid and 0.077 part of *p*-toluene sulphonic acid were mixed and heated for 10 minutes at 280° Centigrade; 14.6 parts of hydroquinone diacetate were then added and heating was continued for 20 minutes at a temperature rising from 250° to 280° Centigrade and at atmospheric pressure and then for 3 hours at 280° Centigrade and at a pressure of 0.5 mm. of mercury. The heating was conducted throughout under oxygen-free nitrogen as in the previous Examples.

The product was drawn into fibres; it softens over the range 220° to 240° Centigrade.

EXAMPLE 5.

4 parts of hexane 1:6 diol diacetate and 16.8 parts of adipic acid were mixed together and heated for 15 minutes at a temperature rising from 250° to 280° Centigrade and at atmospheric pressure. 15.5 parts of hydroquinone diacetate and 0.07 part of *p*-toluene sulphonic acid were then added and heating was continued for 20 minutes at 280° Centigrade and at atmospheric pressure and then for 6 hours at 280° Centigrade and at a pressure of 0.5 mm. of mercury. The heating was conducted throughout under oxygen-free nitrogen as in the previous Examples.

The product was drawn into fibres.

EXAMPLE 6.

2.3 parts of butane 1:4 diol, 16.8 parts of adipic acid and 0.07 part of *p*-toluene sulphonic acid were mixed together and heated for 20 minutes at 220° Centigrade and at atmospheric pressure. 14.6 parts of hydroquinone diacetate were then added and heating was continued for 30 minutes at a temperature rising from 240° to 280° Centigrade and at atmospheric pressure and for 2½ hours at 280° Centigrade and at a pressure of 0.5 mm. of mercury. The heating was conducted throughout under oxygen-free nitrogen as in the previous Examples.

The product was drawn into fibres; it melts within the range 173° to 178° Centigrade.

EXAMPLE 7.

4.1 parts of triethylene glycol diacetate, 15.8 parts of *p,p'*-diacetoxy diphenyl, melting point 161°, prepared by acetylation with acetic anhydride and caustic soda, of *p,p'*-dihydroxy diphenyl, obtained by diazotisation of benzidine (Hirsch, Berichte, 1889, 22, 335), 12.9 parts of adipic acid and 0.06 part of *p*-toluene sulphonic acid were mixed together and heated for 30 minutes at a temperature rising from 200° to 270° Centigrade and at atmospheric pressure

and then for 5 hours at 280° Centigrade and at a pressure of 1 mm. of mercury. The heating was conducted throughout under oxygen-free nitrogen as in the previous Examples.

The product was rubbery at 210° Centigrade and at higher temperatures it could be drawn in fibres.

EXAMPLE 8.

20 parts of dimethyl terephthalate, 9.7 parts of hydroquinone diacetate, 5.2 parts of pentane 1:5 diol, 0.15 part of magnesium methoxide and 0.2 part of aluminium ethoxide were mixed and heated for 80 minutes at a temperature rising from 240° to 280° Centigrade and at atmospheric pressure and then for 2½ hours at 300° Centigrade and at a pressure of 0.3 mm. of mercury. The heating was conducted throughout under oxygen-free nitrogen as in the previous examples.

The product was a buff-coloured high melting polymer.

We are aware that Patent Specification No. 621,102 which, though not published at the date of the present application is of prior date thereto, claims a process for the production of polyesters which comprises heating a free dicarboxylic acid with a diphenol together with acetic phenol.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for the production of mixed polymeric esters which comprises condensing (a) an ω,ω' dicarboxylic acid or terephthalic acid, or an ester or anhydride of such acids, (b) a diester of an aliphatic monocarboxylic acid and an aromatic dihydroxy compound in which the hydroxy groups if on the same benzene nucleus are in the *p* or *m* position with respect to each other, and if on different benzene nuclei are in the *p* and *p'* or *m* and *m'* positions, and (c) an ω,ω' aliphatic dihydroxy compound, or a monoester or diester of such a compound.

2. A process as claimed in claim 1 wherein the diester of the aromatic dihydroxy compound used is a diester of hydroquinone.

3. A process as claimed in claim 1 wherein the diester of the aromatic dihydroxy compound used is a diester of resorcinol.

4. A process as claimed in any of the preceding claims wherein the diester of the aromatic dihydroxy compound used is an ester of the aromatic dihydroxy compound and an aliphatic monocarboxylic acid containing not more than 4 carbon atoms in the molecule.

5. A process as claimed in claim 4 wherein the diester of the aromatic dihydroxy compound used is a diester of the aromatic dihydroxy compound and acetic acid.
6. A process as claimed in any of the preceding claims wherein the ω,ω' dicarboxylic acid used is succinic acid, adipic acid, suberic acid or sebacic acid.
- 10 7. A process as claimed in any of the preceding claims wherein the condensation is effected in the presence of an acid-reacting condensation catalyst.
- 15 8. A process as claimed in claim 7 wherein the catalyst is *p*-toluene sulphonic acid.
9. A process for the production of mixed polyesters as claimed in claim 1 carried out substantially as described in any of the foregoing Examples.
- 20 10. Mixed polyesters when prepared by the process claimed in any of the preceding claims.

Dated this 30th day of November, 1948.

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